

File ID	uvapub:2627
Filename	25462y.pdf
Version	unknown

---

SOURCE (OR PART OF THE FOLLOWING SOURCE):

Type	article
Title	Electron-paramagnetic-resonance study of silver-induced defects in silicon
Author(s)	P.N. Hai, T. Gregorkiewicz, C.A.J. Ammerlaan, D.T. Don
Faculty	FNWI: Van der Waals-Zeeman Institute (WZI)
Year	1997

FULL BIBLIOGRAPHIC DETAILS:

<http://hdl.handle.net/11245/1.132900>

---

*Copyright*

*It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content licence (like Creative Commons).*

---

# Electron-paramagnetic-resonance study of silver-induced defects in silicon

P. N. Hai

*Van der Waals-Zeeman Institute, University of Amsterdam, Valckenierstraat 65-67, NL-1018 XE Amsterdam, The Netherlands  
and Faculty of Physics, National University of Hanoi, 90 Nguyen Trai Street, Hanoi, Vietnam*

T. Gregorkiewicz and C. A. J. Ammerlaan

*Van der Waals-Zeeman Institute, University of Amsterdam, Valckenierstraat 65-67, NL-1018 XE Amsterdam, The Netherlands*

D. T. Don

*Faculty of Physics, National University of Hanoi, 90 Nguyen Trai Street, Hanoi, Vietnam*

(Received 13 November 1996)

In this paper two electron-paramagnetic-resonance spectra are reported in silicon doped with silver in a water vapor atmosphere. These centers, labeled Si-NL56 and Si-NL57, show the orthorhombic-I and trigonal symmetries, respectively, and an effective electron spin  $S=1/2$ . Based on studies with enriched silver isotopes and analysis of the observed twofold hyperfine splitting, the participation of one silver atom is established for both centers. The Si-NL56 center is identified as an isolated substitutional silver atom. Due to the presence of an additional hyperfine interaction with a nuclear spin  $I=5/2$ , the Si-NL57 spectrum is assigned to a complex of silver with another impurity introduced during the diffusion process. Taking into account the sample preparation procedure, the Si-NL57 center is attributed to an  $\text{Al}_i\text{-Ag}_i$  pair in a negative charge state. [S0163-1829(97)02232-7]

## I. INTRODUCTION

In the last ten years the silver dopant in silicon received much attention. This is due to its interesting physical properties as well as to its role in silicon processing. Silver is frequently used as a contact element and as a lifetime killer, similar to gold and platinum, in the fabrication of silicon switching diodes. Adegboyega *et al.*<sup>1</sup> have recently shown that in *p*-type silicon silver forms a deep donor-type center and that its presence leads to a large decrease (by a factor of about 21) of the minority carrier lifetime. It is also known that an undesired silver contamination can give rise to serious problems affecting strongly the electrical properties of devices, especially in metal-oxide-semiconductor structures, due to the fact that it can penetrate the protecting oxide layer of the devices under operating conditions.<sup>2</sup> From a more fundamental point of view, the silver dopant constitutes a particularly interesting case of a transition metal element with a complete  $d^{10}$  electron shell, and is directly comparable to such centers as Au and Pt whose electronic structure is intensively investigated.

A considerable wealth of information on electrical and optical properties of the silver impurity in silicon has been established in the past. Deep-level transient spectroscopy<sup>3,4</sup> (DLTS) revealed deep donor and deep acceptor levels at  $E_v + 0.34$  eV and  $E_c - 0.54$  eV, respectively, and associated them with a silver dopant of amphoteric character. Using photothermal-ionization spectroscopy and Fourier-transform infrared transmission spectroscopy Olajos *et al.*<sup>5</sup> investigated the excitation spectra of electronic excited states in silver-doped silicon and identified those as arising from the deep state of the, probably substitutional, silver donor. Recent photoluminescence measurements showed a dominating Ag-related spectrum with three no-phonon lines in the 780-meV

region associated with the spin-triplet and spin-singlet states of a bound exciton.<sup>6,7</sup>

In spite of the above-mentioned studies, the microscopic structure of the silver-induced centers, which is often revealed by means of electron-paramagnetic-resonance (EPR) spectroscopy, is not clear. In EPR measurements on silver-doped silicon<sup>8,9</sup> a number of silver-related centers has been found. One of the spectra, Si-NL42, has been attributed to a single silver atom in a neutral charge state on a tetrahedral, probably interstitial, site. The issue of the existence of the isolated substitutional silver center in silicon, as postulated from optical and DLTS studies, remains therefore open.

Also interaction of hydrogen with defects in silicon is in the focus of current investigations. Hydrogen, which is a very fast diffuser, can be intentionally incorporated into silicon via implantation, hydrogen plasma exposure, heat treatment at high temperature in the atmosphere of hydrogen gas, and is often present in commercial silicon as a contamination introduced, e.g., by wet etching. Recently it has been shown that also high-temperature heat treatment in water vapor effectively hydrogenates silicon.<sup>10-12</sup> The properties of silicon doped with transition metal (TM) impurities are affected by the presence of hydrogen. It has been established that hydrogen, which can passivate the electrical activity of deep level centers,<sup>11-13</sup> creates complexes with TM impurities. For instance, the formation of a  $\text{Pt-H}_2$  center has been reported.<sup>10,14</sup> In this case hydrogen has been introduced into platinum-doped silicon. A somewhat different situation might be anticipated when hydrogen and TM element are diffused into silicon in one step. One could expect that the presence of hydrogen would not only lead to the generation of TM-hydrogen complexes, but could also affect the diffusion of the TM element. Such effects have been reported for the diffusion of oxygen<sup>15</sup> and aluminum<sup>16</sup> in silicon. In order

to investigate this possibility we have carried out a preliminary test by performing a simultaneous platinum and hydrogen diffusion into a silicon wafer by 3 h annealing at a temperature of 1250 °C in water vapor atmosphere. As a result, the EPR spectrum of the Pt-H<sub>2</sub> pair was obtained and its intensity was similar to that reported previously in samples doped first with Pt (for 70 h) and subsequently heat treated in water vapor.<sup>10</sup> It seems that the platinum diffusion enhancement by hydrogen and the interaction of platinum with hydrogen have taken place in parallel. The method of TM doping in water vapor atmosphere has been used in the current study.

In this paper we present results of an EPR investigation of silicon samples doped with silver in a water vapor environment. In the frame of the study two additional EPR spectra have been detected. While their generation was evidently related to the presence of the (heavy) water vapor, no evidence of a direct hydrogen involvement in the microscopic structure of these centers has been found.

## II. EXPERIMENTAL PROCEDURES

The materials used were boron- and phosphorus-doped, dislocation-free, float-zone silicon crystals with a room-temperature resistivity in the range from 1 to 1000  $\Omega$  cm. The dimensions of samples were typically  $1 \times 1 \times 15$  mm<sup>3</sup> with the length along the [011] crystal direction. The samples were diffused with silver. In this procedure small amounts of natural high-purity silver (99.999%) or monoisotopically enriched (but not high-purity) silver <sup>107</sup>Ag (99.5%) or <sup>109</sup>Ag (99.4%) were deposited on both sides of the sample by scratching. The crystals were then sealed in quartz ampoules containing argon atmosphere and a few milligrams of water. The diffusion treatment was performed in a tube furnace at a temperature of 1250 °C for a duration of about 4 h, and then abruptly terminated by quenching to room temperature. The quenched samples were mechanically lapped to remove the SiO<sub>2</sub> and the silicide surface layer, etched in a mixture of HF and HNO<sub>3</sub>, and then stored in liquid nitrogen until the measurement.

The EPR measurements were performed with a superheterodyne spectrometer operating in the microwave frequency of about 22.9 GHz (*K* band), tuned to dispersion. The sample was mounted with the [011] crystal direction perpendicular to the plane of the rotation of the magnetic field. Most measurements were taken at liquid-helium temperature.

## III. EXPERIMENTAL RESULTS

Following the quenching several new spectra were observed. Figure 1(a) shows typical EPR spectra recorded for a <sup>107</sup>Ag-doped sample, with Fig. 1(b) presenting the corresponding spectra after <sup>109</sup>Ag doping. An anisotropic spectrum, labeled Si-NL56, reproducible for doping with natural or monoisotopically enriched silver, consists of two groups of intense EPR lines corresponding to a twofold hyperfine splitting. In addition to this signal, another anisotropic spectrum, labeled Si-NL57, was also detected in samples for which monoisotopically enriched silver was used as a dopant source. Both spectra could be found only in silver-doped high-resistivity silicon samples (*p* and *n* type). The intensity

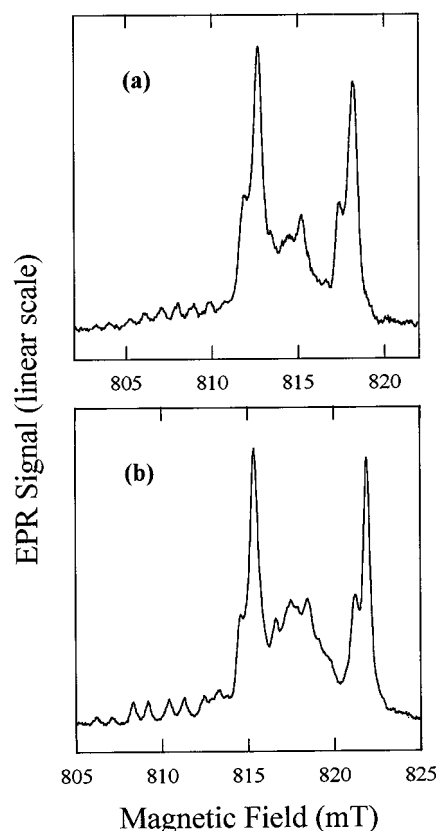


FIG. 1. The anisotropic EPR spectra observed 2.5° away from the [011] direction in the (011) plane for a sample doped with (a) <sup>107</sup>Ag (microwave frequency  $\nu = 22.7838$  GHz) and (b) <sup>109</sup>Ag ( $\nu = 22.8697$  GHz) silver isotopes, at temperature  $T = 4.2$  K.

of the Si-NL57 spectrum was smaller by about a factor 15 than that of the Si-NL56 spectrum. Further, the two spectra have a different temperature dependence: the Si-NL57 spectrum vanishes when the temperature is increased to 8 K, whereas the Si-NL56 spectrum remains practically unaffected. This shows that the two spectra belong to different defect centers. In what follows both spectra will be discussed separately.

### A. Si-NL56 center

Two most intense groups of EPR lines of this spectrum behave identically with conditions of observation and correspond to a twofold hyperfine splitting due to the interaction of an effective electron spin  $S = 1/2$  and a nuclear spin  $I = 1/2$  with an abundance of 100%. Taking into account the elements with such an isotopic composition and the fact that the anisotropic spectrum could only be produced when diffusing silver in the water vapor ambient at high temperature, we consider silver or/and hydrogen as the possible candidate(s) responsible for the twofold splitting. To examine the role of hydrogen and silver in the defect formation, two additional sets of different samples were prepared: the first set of samples was doped with natural (high-purity) or monoisotopically enriched silver in the atmosphere of argon gas only; the second set was heated without silver in the ambient of water vapor. The heat-treatment parameters were kept identical in both cases. No Si-NL56 EPR spectrum was detected.

From these observations we conclude that both hydrogen and silver are needed in the formation process of this center. In view of the relatively low intensity of the Si-NL56 spectrum, electron nuclear double resonance could not be applied for identification of the origin of the hyperfine splitting. Therefore in order to clarify the presence of hydrogen and silver in the defect structure, several samples were prepared with the use of silver and heavy water vapor ( $D_2O$ , with nuclear spin  $I=1$  for deuterium). The heat treatment and the quenching rate were kept unchanged. No differences between samples doped with silver in the atmosphere of water and heavy water vapor have been found. This leaves silver as the prominent candidate for the explanation of the hyperfine structure. A similar sample doped with the enriched silver isotope  $^{109}Ag$  was prepared. The Si-NL56 spectrum could be detected again, as shown in Fig. 1(b). The distinct difference in the hyperfine splitting, as depicted in Figs. 1(a) and 1(b), can be seen. The ratio between the splittings observed in the experiment is equal to 0.87, and perfectly matches the ratio of the nuclear magnetic moments of the two isotopes:  $\mu = -0.1135\mu_N$  for  $^{107}Ag$  and  $\mu = -0.1305\mu_N$  for  $^{109}Ag$ .<sup>17</sup> On the basis of these isotope effects on the spectra we conclude that the anisotropic Si-NL56 center involves a single silver atom. While hydrogen is not observed as a structural component of the Si-NL56 center, it takes part in its formation process.

The spectrum could be fitted with the spin Hamiltonian

$$\mathcal{H}_S = \mu_B \vec{B} \cdot \vec{g} \cdot \vec{S} + \vec{S} \cdot \vec{A} \cdot \vec{I}, \quad (1)$$

where  $\vec{g}$  and  $\vec{A}$  represent the Zeeman splitting and the hyperfine interaction tensors, respectively, with the electron spin  $S=1/2$  and nuclear spin  $I=1/2$ . Full angular dependence of the spectrum was obtained when rotating the external magnetic field in the (011) crystal plane, with the result as given in Fig. 2. This angular dependence could be fitted satisfactorily with a  $\vec{g}$  tensor and a hyperfine interaction tensor  $\vec{A}$  of orthorhombic-I symmetry ( $C_{2v}$ ). The results of the computer fit for the Si-NL56 center are summarized in Table I. For an easy comparison the parameters of the isolated substitutional platinum center ( $Pt_s^-$ ) (Refs. 18,19) and the Si-NL50 center, whose identification with an isolated substitutional gold center ( $Au_s^0$ ) has been suggested,<sup>20</sup> are also included in the table, since both  $Pt_s^-$  and  $Au_s^0$  are isoelectronic to silver; the identification of the Si-NL50 center with  $Au_s^0$  is, however, controversial.<sup>21</sup> As can be concluded, the  $\vec{g}$  tensor and the hyperfine interaction tensor of the Si-NL56 center are clearly different from those of the previously identified isolated silver (Si-NL42) and silver-related centers.<sup>8,9</sup>

In this study, due to the simultaneous presence of the Si-NL57 spectrum, hyperfine interactions with  $^{29}Si$  could not be identified.

### B. Si-NL57 center

The second anisotropic spectrum, Si-NL57, was found to accompany the Si-NL56 in high-resistivity silicon samples doped with the isotopically enriched silver, as shown in Figs. 1(a) and 1(b). (The spectrum was not observed when natural high-purity silver was used for doping). The trigonal symmetry of this center is evident from its angular dependence in

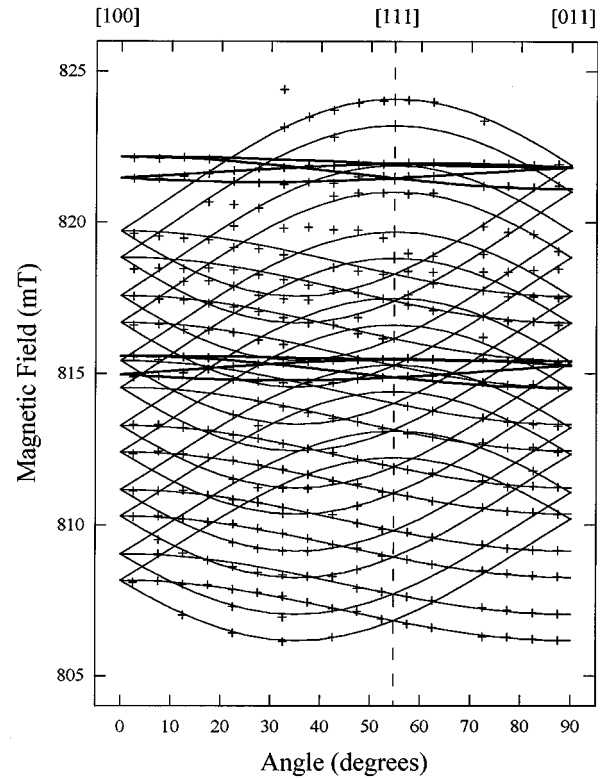


FIG. 2. Angular dependence of the Si-NL56 and Si-NL57 spectra measured for the  $^{109}Ag$ -doped sample. The bold and thin solid lines represent fits to the experimental data (+) according to Eq. (1) for spectrum Si-NL56 and Eq. (2) for Si-NL57, respectively. The microwave frequency is  $\nu = 22.8697$  GHz.

the (011) crystal plane depicted in Fig. 2. The spectrum intensity varies with the angle and is about one order of magnitude smaller than that of the Si-NL56 center. The observed spectrum is not very well resolved, and overlaps partially with the Si-NL56. It contains six groups of EPR lines consistent with the sixfold hyperfine splitting due to an interaction of an effective electron spin  $S=1/2$  with a nuclear spin  $I=5/2$  with an abundance of 100%. Further twofold splitting within a line group can be explained by the hyper-

TABLE I. Spin-Hamiltonian parameters of the Si-NL56 center. Respective values for the  $Pt_s^-$  and Si-NL50 defects are given for comparison.

Center	Tensor	Principal values			Unit	Reference
		$  [100]$	$  [011]$	$  [0\bar{1}1]$		
$Pt_s^-$ ( $^{195}Pt$ )	$\vec{g}$	2.0789	1.3867	1.4266		18,19
	$\vec{A}$	379.3	439.5	550.8	MHz	
Si-NL50 ( $^{197}Au$ ) <sup>a</sup>	$\vec{g}$	2.3015	1.9956	2.0752		20
	$\vec{A}$	18.88	6.32	5.36	MHz	
	$\vec{Q}$	3.26	-2.67	-0.59	MHz	
Si-NL56 ( $^{107}Ag$ ) ( $^{109}Ag$ )	$\vec{g}$	1.9954	1.9960	1.9980		This work
	$\vec{A}$	160.0	155.5	159.4	MHz	
	$\vec{A}$	184.3	179.2	183.7	MHz	

<sup>a</sup>For a discussion on the identification, see the text.

TABLE II. Spin-Hamiltonian parameters of the Si-NL57 center. The hyperfine components are given in MHz.

Element	$^{107}\text{Ag}$	$^{109}\text{Ag}$	$^{27}\text{Al}$
$g_{\parallel}$		1.9971	
$g_{\perp}$		2.0127	
$A_{\parallel}$	21.4	24.7	61.4
$A_{\perp}$	21.4	24.7	59.2

fine interaction with a nuclear spin  $I = 1/2$  with an abundance of 100%. This spectral structure indicates a complex consisting of two different impurity atoms. Similar to the previously discussed Si-NL56 spectrum, the twofold hyperfine splitting could be caused either by hydrogen or by silver in view of their presence in the samples. However, also in this case identical spectra are obtained regardless of whether water ( $\text{H}_2\text{O}$ ) or heavy water ( $\text{D}_2\text{O}$ ) vapor atmosphere is used. On the other hand, the ratio of the magnetic-field doublet splittings observed for the samples doped with enriched  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  is consistent with the ratio of the nuclear magnetic moments of the two isotopes. We therefore conclude on the involvement of one silver atom in the defect structure of this center. With the nuclear spin  $I = 5/2$ , the other component of the complex has to be considered as a contaminant introduced by diffusion. One can note that the Si-NL57 spectrum was not present in samples doped with high-purity natural silver. There are several elements with  $I = 5/2$  and a 100% natural abundance:  $^{27}\text{Al}$ ,  $^{55}\text{Mn}$ ,  $^{127}\text{I}$ ,  $^{141}\text{Pr}$ , Re (with two isotopes having roughly identical nuclear magnetic moments). Out of these, I, Pr, and Re can be excluded as rare contaminants in silicon. In order to identify the second component several samples were prepared under the same conditions and with a very small amount of Mn. The Si-NL57 spectrum could not be observed in such cases. Instead, the well-known  $\text{Mn}_i^-$  spectrum and another Mn-related spectrum were always dominating.<sup>22</sup> In this way Mn has been ruled out as a possible constituent of the Si-NL57 center. On the other hand, the Si-NL57 spectrum could be readily seen in samples prepared under the same conditions and codoped with natural high-purity silver (99.999%) and aluminum. We note further that the isotopically enriched silver used in our experiments was indicated to have a considerable Al contamination. In view of the above facts we assume that Al is involved in the defect composition and propose to assign the Si-NL57 spectrum to an Al-Ag pair.

The experimental data could be fitted using the spin Hamiltonian

$$\mathcal{H}_S = \mu_B \vec{B} \cdot \mathbf{g} \cdot \vec{S} + \vec{S} \cdot \mathbf{A}_{\text{Al}} \cdot \vec{I}_{\text{Al}} + \vec{S} \cdot \mathbf{A}_{\text{Ag}} \cdot \vec{I}_{\text{Ag}}, \quad (2)$$

where  $\mathbf{g}$ ,  $\mathbf{A}_{\text{Al}}$ , and  $\mathbf{A}_{\text{Ag}}$  represent the Zeeman splitting tensor and the hyperfine interaction tensors for Al and Ag, respectively, with the effective electron spin  $S = 1/2$ . The results of the computer fit are listed in Table II. The hyperfine splitting due to Ag is almost isotropic. The obtained principal  $g$  values with  $g_{\parallel} = 1.9971$  and  $g_{\perp} = 2.0127$  are close to the spin-only value  $g_e = 2.00232$ . Therefore we can exclude the possibility that the observed spectrum could arise from the resonance in the ground-state doublet of a true spin quartet

$S = 3/2$ , split by a trigonal crystal field. For the aluminum hyperfine interaction we find  $a = 59.9$  MHz and  $b = 0.7$  MHz as its isotropic and anisotropic parts, respectively. Applying the conventional one-electron linear-combination of atomic-orbitals (LCAO) treatment to analyze the experimentally determined hyperfine interaction components for the localization of the paramagnetic electron on aluminum and silver nuclei, the spin densities  $\eta^2 \alpha^2$  and  $\eta^2 \beta^2$  in the  $3s$  and  $3p$  orbitals on the aluminum atom are then determined as 1.6% and 0.8%, respectively. For the silver atom only the isotropic part of the hyperfine interaction is detected resulting in the spin density  $\eta^2 \alpha^2$  in the  $5s$  orbital of 1.6%.

## IV. DISCUSSION

### A. Si-NL56 center

Copper, silver, and gold atoms have similar free-atom electronic configurations in vacuum with one  $ns$  electron outside a closed  $(n-1)d$  shell ( $n = 4, 5$ , and  $6$  for Cu, Ag, and Au, respectively). The same applies to platinum in the negative charge state  $\text{Pt}^-$ , which is isoelectronic to  $\text{Au}^0$ . Therefore a similar kind of symmetry in the isolated substitutional site could be expected for all of them. In fact several experimental results were shown to support the idea. The EPR data for the isolated substitutional platinum  $\text{Pt}_s^-$  reported by Woodbury and Ludwig<sup>18</sup> revealed the orthorhombic-I ( $C_{2v}$ ) symmetry with the electron spin  $S = 1/2$ . Also for gold in silicon an orthorhombic-I spectrum [Si-NL50 (Ref. 20)] has been reported, although its relation to an isolated neutral gold atom is under dispute and requires further confirmation. In the IR absorption measurements for silver-doped silicon<sup>5</sup> the observation of four lines for the  $1s(E+T_2)$  multiplet indicates that the center has orthorhombic-I ( $C_{2v}$ ) symmetry (or lower). Based on the vacancy model<sup>23</sup> this spectrum was then postulated to arise from a neutral substitutional silver dopant. From these findings, it seems reasonable to conclude that the common trend for the symmetry of these impurities in the isolated substitutional site in silicon is the orthorhombic-I.

Following the observation of the isotope effect, as outlined in the preceding section, we concluded on the participation of a single silver atom in the structure of the orthorhombic-I Si-NL56 center reported here. At the same time the isotope effects on the spectra do not support the possibility that the center consists of a pair of silver and hydrogen atoms. Also a pair of silver and an impurity with zero nuclear magnetic moment seems improbable, although such a possibility cannot be ruled out experimentally. Therefore we suggest that the Si-NL56 spectrum of the orthorhombic-I symmetry arises from an isolated substitutional silver atom. From Table I one can see that the obtained principal values of the Zeeman splitting and hyperfine interaction tensors of this center are nearly isotropic, with a small distortion. Such a distortion from the high-symmetry site of the whole defect configuration is in agreement with the theoretical expectation and supports the model. Our identification is also consistent with the results of photoluminescence measurements performed on the same samples: the dominating  $A, B, C$  lines assigned to an isolated silver atom and some other silver-related features similar to those reported in Refs. 5–7 were detected.

In a previous work on EPR of silver-doped silicon, Son *et al.*<sup>8</sup> attributed the Si-NL42 spectrum to a neutral isolated silver atom on a high-symmetry interstitial site. The assignment followed from the fact that the observed hyperfine interaction was small ( $A = 4.76$  MHz for  $^{107}\text{Ag}$ ) as compared to the Fermi contact term for the Ag  $5s$  orbital  $A_c = -1831$  MHz.<sup>24</sup> For the hyperfine interactions found presently the fraction of spin density in the  $5s$  orbital on the silver atom in the Si-NL56 center is about 30 times bigger than that found for the cubic Si-NL42 center. If we relate both spectra to an isolated silver atom, these results suggest a different lattice site in the two cases; taking into account the spin density it seems natural to assign an interstitial site for the Si-NL42 center, and a substitutional one for the Si-NL56. With the current findings the microscopic picture of an isolated silver impurity in silicon becomes complete. It bears also a close similarity to the behavior of nickel in silicon: the isolated interstitial nickel  $\text{Ni}_i^+$  in the high-symmetry site<sup>25</sup> and the isolated substitutional nickel  $\text{Ni}_s^-$  of the orthorhombic-I symmetry.<sup>26</sup>

The Si-NL56 spectrum, with the orthorhombic-I symmetry, the electron spin  $S = 1/2$ , the principal  $g$  values close to the spin-only value  $g_e = 2.00232$ , and the nearly  $[011]$  axial hyperfine interaction, (i.e., similar to the case for the isolated vacancy  $\text{V}^-$  in silicon<sup>27</sup>), is in good agreement with the vacancy model proposed by Watkins.<sup>23</sup> Following this model, the substitutional silver atom in its neutral charge state has a completely filled  $4d$  shell accommodating 10 electrons ( $4d^{10}$ ). The unpaired  $5s$  electron, responsible for the paramagnetism of the center, occupies the  $b_1$  orbital of the vacancy  $t_2$  gap manifold state, which is split due to a Jahn-Teller distortion. Applying the treatment by Anderson, Ham, and Watkins<sup>28</sup> developed for the vacancy model, with the anisotropic term of the hyperfine interaction  $P = -176.4$  MHz for a  $^{107}\text{Ag}$   $4d$  orbital,<sup>29</sup> we find that the experimental value of  $A_{[0\bar{1}1]} - (A_{[100]} + A_{[011]})/2 = +1.65$  MHz corresponds to the  $N^2 \approx 1.2\%$  percentage of  $d$  character in the orbital. This value is in good agreement with the spin-density value of 2.8% for the  $4d$  orbital on the silver atom found alternatively in the numerical analysis of the experimental hyperfine interaction based on the LCAO approximation. Such a localization value is reasonable within the vacancy model.

Finally, we comment on a possible role of H (or D) in the formation of the Si-NL56 center. The heat treatment at high temperature in the (heavy) water vapor ambient was shown to effectively introduce H (or D) into silicon; H (or D) was found either to passivate effectively the defect and impurity centers,<sup>11,12</sup> and/or to create new complexes with impurity atoms<sup>10</sup> through the bulk of the samples. In either case, hydrogen plays an important role in the microscopic structure of thus formed defects. Also in the current case the presence of hydrogen in the samples after the diffusion process is unquestionable. However, as pointed out before, no involvement of hydrogen in the Si-NL56 center has been found, while hydrogen was required in its formation process. This situation is somewhat similar to the case of two Au-Au defects recently reported by Williams *et al.*<sup>30</sup> In view of the available evidence we suggest that hydrogen promotes the substitutional diffusion mechanism of silver. If further con-

firmed, this would be an observation of the hydrogen-related enhancement of diffusion for a transition-metal impurity in silicon.

### B. Si-NL57 center

Based on the observed hyperfine interactions we propose to identify the Si-NL57 center as an Al-Ag pair. Obviously, the trigonal symmetry of the pair requires two atoms located along  $\langle 111 \rangle$ , possibly on the nearest-neighbor sites. In non-irradiated silicon, aluminum is known to occupy substitutional sites and acts as a shallow acceptor. Thus, unless the material is strongly  $p$  type, it will form the  $\text{Al}_s^-$  center, resulting in a spin  $S = 0$ . Therefore the observed electron spin  $S = 1/2$  of the Si-NL57 center has to arise from the silver component. From the analysis of the experimental results, one can see that the hyperfine interaction with the silver atom is isotropic and, as such, results from the localization of the unpaired spin predominantly in the  $5s$  orbital. This situation corresponds to the  $4d^{10}5s^1$  electronic configuration of a silver atom in which the  $4d$  shell is complete and an unpaired electron in the  $5s$  shell gives rise to the electron spin  $S = 1/2$ , in compliance with the observed spin  $S = 1/2$  of the center formed by coupling of aluminum and silver spins. As discussed for the Si-NL56 spectrum, both  $\text{Ag}_i^0$  and  $\text{Ag}_s^0$  isolated silver centers have the required electronic configuration. However, in view of the results obtained for the Si-NL56 center and the general trend of  $(n-1)d^{10}ns^1$  type impurities outlined earlier, a neutral silver atom on a substitutional site is likely to undergo a tetragonal Jahn-Teller and a weaker trigonal distortion, so that the overall symmetry of the hypothetical  $\text{Al}_s^- - \text{Ag}_s^0$  pair would be orthorhombic-I, or lower. Since the observed symmetry of the Si-NL57 center is trigonal, the  $\text{Al}_s^- - \text{Ag}_s^0$  pair is not a good candidate for the microscopic model of this defect. On the other hand, the  $\text{Al}_s^- - \text{Ag}_i^0$  pair will be trigonal and therefore in agreement with the experimental findings. Based on this reasoning, we attribute the Si-NL57 spectrum to the  $\text{Al}_s^- - \text{Ag}_i^0$  pair in the negative charge state. One notes that several other silver-related pairs of trigonal symmetry have been reported before.<sup>8,9</sup>

Since the Si-NL57 spectrum was only observed for the samples doped with isotopically enriched silver which was contaminated with aluminum, and not when natural silver of high purity (99.999%) was used, we conclude that Al ions were introduced into silicon during the heat treatment. Aluminum, similar to other group-III acceptors, is known to be a slow diffuser in silicon with the activation energy  $Q = 2.85$  eV.<sup>31</sup> We point out, however, that in this case the diffusion process of Al could be influenced by three additional factors: (i) a simultaneous presence of Ag, which is known to create vacancies,<sup>25</sup> and therefore promotes the substitutional diffusion mechanism; (ii) the oxidation of the sample surface, which took place in water vapor atmosphere at  $1250^\circ\text{C}$  temperature, and which also enhances the diffusion;<sup>32</sup> (iii) the presence of hydrogen atoms which could affect the activation energy for diffusion. In any case, a low concentration of aluminum contamination is consistent with the low intensity of the Si-NL57 spectrum observed in this study.

## V. CONCLUSION

The isolated substitutional silver atom in silicon has been identified and analyzed by the EPR technique. The experimental data could be satisfactorily explained within the vacancy model. In addition to that an EPR spectrum associated with the  $\text{Al}_s^-$ - $\text{Ag}_i^0$  pair has been reported. Also the

hydrogen-enhanced diffusion of aluminum, platinum, and silver in silicon has been observed.

## ACKNOWLEDGMENTS

P.N.H. acknowledges the Faculty of Mathematics, Informatics, Physics, and Astronomy, University of Amsterdam for financial support in the Van der Waals-Zeeman Institute.

- <sup>1</sup>G. A. Adegboyega, L. Passari, M. A. Butturri, and E. Susi, *Phys. Status Solidi A* **156**, 169 (1996).
- <sup>2</sup>S. Kar and R. Varghese, *J. Appl. Phys.* **53**, 4435 (1982).
- <sup>3</sup>N. Baber, H. G. Grimmeiss, M. Kleverman, P. Omling, and M. Z. Iqbal, *J. Appl. Phys.* **62**, 2853 (1987).
- <sup>4</sup>V. Pandian and V. Kumar, *Phys. Status Solidi A* **109**, 273 (1988).
- <sup>5</sup>J. Olajos, M. Kleverman, and H. G. Grimmeiss, *Phys. Rev. B* **38**, 10 633 (1988).
- <sup>6</sup>I. de Maat-Gersdorf, T. Gregorkiewicz, and C. A. J. Ammerlaan, *Mater. Sci. Forum* **143-147**, 755 (1994).
- <sup>7</sup>N. T. Son, M. Singh, J. Dalfors, B. Monemar, and E. Janzén, *Phys. Rev. B* **49**, 17 428 (1994).
- <sup>8</sup>N. T. Son, V. E. Kustov, T. Gregorkiewicz, and C. A. J. Ammerlaan, *Phys. Rev. B* **46**, 4544 (1992).
- <sup>9</sup>N. T. Son, T. Gregorkiewicz, and C. A. J. Ammerlaan, *J. Appl. Phys.* **73**, 1797 (1993).
- <sup>10</sup>M. Höhne, U. Juda, Yu. V. Martynov, T. Gregorkiewicz, C. A. J. Ammerlaan, and L. S. Vlasenko, *Phys. Rev. B* **49**, 13 423 (1994).
- <sup>11</sup>Yu. V. Martynov, T. Gregorkiewicz, and C. A. J. Ammerlaan, *Phys. Rev. Lett.* **74**, 2030 (1995).
- <sup>12</sup>I. S. Zevenbergen, T. Gregorkiewicz, and C. A. J. Ammerlaan, *Phys. Rev. B* **51**, 16 746 (1995).
- <sup>13</sup>S. J. Pearton, J. W. Corbett, and M. Stavola, *Hydrogen in Crystalline Semiconductors* (Springer-Verlag, Berlin, 1992).
- <sup>14</sup>P. M. Williams, G. D. Watkins, S. Uftring, and M. Stavola, *Phys. Rev. Lett.* **70**, 3816 (1993).
- <sup>15</sup>S. K. Estreicher, *Phys. Rev. B* **41**, 9886 (1990).
- <sup>16</sup>Yu. V. Gorelinskii, Kh. A. Abdullin, and B. N. Mukashev, in *Shallow-Level Centers in Semiconductors*, edited by C. A. J. Ammerlaan and B. Pajot (World Scientific, Singapore, 1997), p. 315.
- <sup>17</sup>G. H. Fuller, *J. Phys. Chem. Ref. Data* **5**, 835 (1976).
- <sup>18</sup>H. H. Woodbury and G. W. Ludwig, *Phys. Rev.* **126**, 466 (1962).
- <sup>19</sup>F. G. Anderson, R. F. Milligan, and G. D. Watkins, *Phys. Rev. B* **45**, 3279 (1992).
- <sup>20</sup>N. T. Son, T. Gregorkiewicz, and C. A. J. Ammerlaan, *Phys. Rev. Lett.* **69**, 3185 (1992).
- <sup>21</sup>G. D. Watkins, M. Kleverman, A. Thilderkvist, and H. G. Grimmeiss, *Phys. Rev. Lett.* **67**, 1149 (1991).
- <sup>22</sup>P. N. Hai, T. Gregorkiewicz, C. A. J. Ammerlaan, and D. T. Don (unpublished).
- <sup>23</sup>G. D. Watkins, *Physica B & C* **117B&118B**, 9 (1983).
- <sup>24</sup>J. R. Morton and K. F. Preston, *J. Magn. Reson.* **30**, 577 (1978).
- <sup>25</sup>G. W. Ludwig and H. H. Woodbury, in *Solid State Physics: Advances in Research and Applications*, edited by F. Seitz and D. Turnbull (Academic, New York, 1962), Vol. 13, 223.
- <sup>26</sup>L. S. Vlasenko, N. T. Son, A. B. van Oosten, C. A. J. Ammerlaan, A. A. Lebedev, E. S. Tapygov, and V. A. Khrantsov, *Solid State Commun.* **73**, 393 (1990).
- <sup>27</sup>M. Sprenger, S. H. Muller, E. G. Sieverts, and C. A. J. Ammerlaan, *Phys. Rev. B* **35**, 1566 (1987).
- <sup>28</sup>F. G. Anderson, F. S. Ham, and G. D. Watkins, *Phys. Rev. B* **45**, 3287 (1992).
- <sup>29</sup>A. K. Koh and D. J. Miller, *At. Data Nucl. Data Tables* **33**, 235 (1985).
- <sup>30</sup>P. M. Williams, P. W. Mason, and G. D. Watkins, *Phys. Rev. B* **53**, 12 570 (1996).
- <sup>31</sup>M. Chang, *J. Electrochem. Soc.* **128**, 1987 (1981).
- <sup>32</sup>S. Mizuo and H. Higuchi, *Jpn. J. Appl. Phys.* **21**, 56 (1982).